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A relationship between the geometrical structure of a nanoporous metal foam and its modulus

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Abstract

One of the crucial characteristics of a porous medium is its relative density ρ^*, i.e. the volume fraction of the solid. For example, in low density foams ($\rho^* < 0.1$) the macroscopic material properties depend on the foam geometry only through the relative density. The relative density of nanoporous (NP) metal foams synthesized by dealloying is typically in the range $\rho^* \geqslant 0.4$. This places NP metal foams in a previously unexplored parameter regime and necessitates reexamination of scaling laws derived for low density foams. In this work we demonstrate that the modulus of NP metal foams does not exhibit a clear correlation with the relative density. We trace this apparent disagreement with existing scaling laws to the agglomeration of mass in the junctions. We then derive and verify a new scaling relationship for the dependence of relative density and relative modulus on the geometric parameters such as strut thickness, length and junction size. We find good agreement between our model and experimental measurements for single crystal gold NP foams with large junction sizes. In contrast, polycrystalline NP platinum with nanosized grains within the struts shows an enhancement in the modulus that cannot be attributed to the foam geometry only. Based on this analysis, we infer a more than an order of magnitude enhancement of the modulus of the nanograined Pt struts compared to bulk platinum.

Keywords: Nanoporous; Metals; Scaling; Density; Modulus

1. Introduction

Nanoporous (NP) metal foams possess high surface-to-volume ratios and show great promise as components of fuel cells [1,2] and sensors. These systems have been suggested for use in biological applications, for example as antimicrobial scaffolds [3] or platforms on which to explore biological material behavior [4]. NP metal foams are often synthesized by dealloying, whereby the less noble elements in an alloy are selectively dissolved in the electrolyte, leaving behind the more noble elements to self-assemble into struts with characteristic dimension in the range 2–100 nm [1,3,5–8]. The struts are interconnected in space, forming an open cell foam.

At present, the structure–property relationship of NP metal foams is not well understood. For open cell foams of low density, such relationships have been examined using dimensional analysis [9–11]. For example, the relative density, i.e. the solid fraction of the foam, relates to strut geometry as $\rho^* \propto (t/l)^2$, where t and l are the strut thickness and length, respectively. In turn, the deformation of a single strut can be used to obtain information of the collective foam response. For example, under the assumption that a strut deforms mainly in bending, the relative foam modulus (E_f/E_s) can be found to scale as $E_f/E_s \propto (t/l)^4$, where E_f is the foam modulus and E_s is the modulus of a solid strut. By noting that both the relative modulus and relative density are functions of the same geometric parameters, it has been shown that

$$E_f/E_s \propto (\rho^*)^2 \tag{1}$$

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For low density foams ($\rho^* < 0.1$), Eq. (1) agrees well with experimental measurements [9]. In contrast, the validity of this scaling law has not been established for NP metal foams which are typically characterized by larger ρ^*. Some researchers find reasonable agreement of Eq. (1) with experimental data (e.g. Ref. [12]), while others observe an enhancement in the modulus of NP metal foams that scales with strut thickness (e.g. Ref. [13]). To further illustrate this point, we summarize in Fig. 1 available experimental measurements of the relative modulus and relative density for NP metal foams and compare them against the prediction of Eq. (1). It is immediately apparent that there exists little correlation between relative density and the relative modulus.

In principle, the deviation of the observed properties of NP metal foams from simple scaling relations such as Eq. (1) may be expected. While NP metal foams possess some similarities with open cell foams at larger length scales, their properties are expected to be greatly influenced by the nanoscale size of their geometrical features (e.g. struts and pores). For example, the free surfaces in NP metals may be expected to be energetically important, hence playing a bigger role in controlling the properties of the foam compared to bulk foams [14,15]. Another complexity may arise when nanosized geometrical features are in the same range as the material internal scales, e.g. size of grains [8].

While it is tempting to attribute the NP metal foam behavior summarized by Fig. 1 to the aforementioned size effects at the nanoscale, the validity of the scaling laws themselves for NP metal foams has not been firmly established. Indeed, as we discuss in this paper the relative density of NP metal foams is $\rho^* > 0.4$ and occupies a different parameter space compared to bulk metal foams. It is important to establish scaling laws for the larger relative densities so as to correctly separate nanosize effects from those due to geometry. In this paper we set out to understand why the data for the relative modulus of NP metal foam exhibit no correlation with relative density and to examine whether this disagreement originates from essentially nanoscale effects or whether the scaling relationship itself needs to be modified (see Section 4 for details).

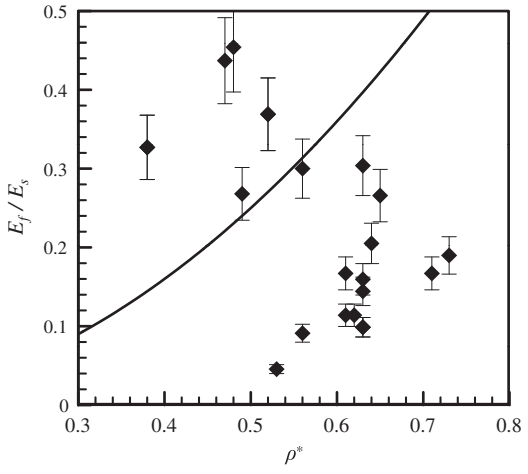

Fig. 1. Relative modulus as a function of the relative density. The solid line represents scaling law (Eq. (1)). Symbols represent material systems of NP Au and NP Cu from the literature and our own data on NP Pt. Details of the experimental measurements can be found in Sections 2 and 3. The data are summarized in Tables 1 and 2.

In a recent work we demonstrated that inherent dimensional changes (shrinkage) occur during synthesis of NP metals by dealloying. These changes may lead to an underestimation of the relative density and thus cause erroneous correlation with properties [16]. In this work we measure relative density using stereographic projections from electron micrographs and validate these measurements using Rutherford backscattering spectrometry (RBS). We also use the micrographs to obtain statistical information on the strut geometry (strut diameter, length, etc.). This allows us to closely examine the relation between relative density and strut geometry. Surprisingly, we find that the simple dimensional analysis result $\rho^* \propto (t/l)^2$ does not describe the behavior of NP metal foams, especially for low t/l ratios. Closer examination of NP metal structure reveals a possible cause for this discrepancy, namely agglomeration of mass at junctions.

We propose a modification to the dimensional analysis that includes a correction for mass agglomeration. We use this simple model to obtain an expression for the scaling of NP metal modulus with strut geometry. We note that the effect of mass agglomeration at junctions has been studied for low density foams using finite elements and was found to have little effect on the modulus [17]. In our analysis we find that this effect becomes considerable for large t/l ratios and may lead to a 100% increase in modulus. We find good agreement between the model and experimental observations for single crystal NP metal samples with large junctions and large strut thicknesses. We then compare the modified scaling relationship to the measurements of modulus in more complex NP metal foams that have nanosized grains within the struts. We find that the observed relative modulus is greatly enhanced compared to the model prediction. This strongly indicates that the enhancement of the relative modulus in these cases is not a geometric effect, but rather can be attributed to the effects of the internal structure.

This paper is divided into the following parts: Section 2 is a description of the experimental protocol followed for the relative density and modulus measurements for NP metal foams, and Sections 3 and 4 present the results for relative density and the modulus as a function of thickness to strut ratio, respectively.

2. Experimental methodology

We synthesized open cell NP platinum (Pt) foam for a range of densities and examined the strut morphology. The sample preparation procedure and the characterization techniques are presented here. In addition to our own measurements, we include results that have been reported in the